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Viscometry Constants for 1,4 Polybutadiene in Tetralin at 135C

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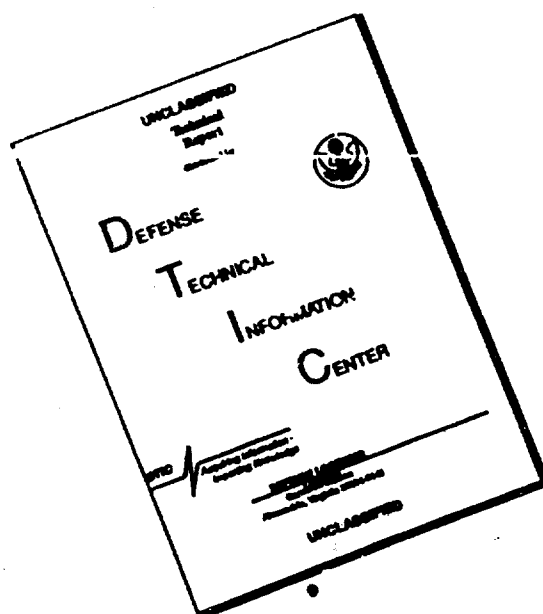
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Viscometry Constants for 1,4 Polybutadiene in Tetralin at 135°C

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Abstract: Mark-Houwink K and a parameters were obtained for 1,4 polybutadiene (PBD) in tetralin at 135°C via viscometry tests on a set of PBD standards ranging in molecular weight from 5,000 g/mol to 240,000 g/mol. Values for K and a are 0.0161 ± 0.0025 ml/g and 0.74, respectively, for analysis based on specific viscosity, and 0.0145 ± 0.0022 ml/g and 0.75 for analysis based on relative viscosity.

For linear-chain polymers,

$$[\eta] = K * (M_v)^a \quad (1)$$

where $[\eta]$ is intrinsic viscosity, K and a are Mark-Houwink parameters for a given polymer in a specified solvent at a specified temperature, and M_v is the viscosity average molecular weight. Thus if $[\eta]$, K , and a are known, M_v can be calculated. Or if $[\eta]$ is measured for a series of standards with known molecular weights, M , then a and $\log K$ are obtained from a plot of $\log [\eta]$ vs. $\log M$.

During the course of a research program on blends of crystallizable polybutadiene (PBD) isomers [1, 2], we needed to determine the molecular weight of a trans 1,4 polybutadiene sample. Gel Permeation Chromatography (GPC) of the trans 1,4 PBD in 140°C tetralin was unsuccessful due to extensive polymer degradation during testing. Therefore, we obtained Mark-Houwink constants for a series of 1,4 PBD (mixed cis/trans) standards of known molecular weight and low polydispersities. The constants were determined using solutions of PBD in tetralin at 135°C, and then we obtained the M_v of the trans 1,4 PBD sample.

The series of 1,4 PBD standards had molecular weights of 5000, 23000, 150000, and 240000 g/mol (American Polymer Standards Corporation, Mentor, OH). The standards were reported to have polydispersities of 1.1-1.3 and microstructures with approximately 42% cis 1,4, 50% trans 1,4, and 8% 1,2 repeat units.

The intrinsic viscosity $[\eta]$ is the y-intercept on a plot of η_{sp}/c or $\ln(\eta_r)/c$ as a function of c (concentration), where $\eta_r = \eta/\eta_0$ is the relative viscosity and $\eta_{sp} = (\eta - \eta_0)/\eta_0 = \eta_r - 1$ is the specific viscosity; in these

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relationships, η is the sample viscosity and η_0 is the viscosity of the solvent [3]. It is usually reasonable to approximate the quantity η/η_0 by t/t_0 , where t is the time for a polymer solution to pass between two marks on an appropriate viscometer and t_0 is the time for pure solvent to pass between the same marks. This approximation breaks down at low values of t where a kinetic energy correction is required [3, 4]. It is also possible to use a series of viscometers to obtain data at various flow (shear) rates and thereby extrapolate to zero shear rate conditions. We report data here which are uncorrected for the effects of kinetic energy and finite shear rate.

A Cannon-Fenske viscometer (size 150), was used for all of our viscometry tests. The viscometer was placed in a stirred oil bath at $135^\circ \pm 2^\circ \text{C}$. Sample solutions were prepared and tested in 10 ml of tetralin. Immediately prior to the test, solutions were mixed at 135°C for at least thirty minutes. Between runs, the viscometer was rinsed with 10 ml of tetralin until t_0 was reproducible at 19.7 ± 0.2 seconds. At least four concentrations were tested for each 1,4 PBD standard, as listed in Table 1. The concentrations were selected to give approximately $1.2 < t/t_0 < 2.0$.

The higher molecular weight 1,4 PBD standards (150,000 and 240,000 g/mol) degraded with time in the hot tetralin. The flow times, t , became progressively shorter as the solutions remained at 135°C over the course of approximately 30 minutes, even when Irganox 1076 antioxidant (Ciba-Geigy Corporation, Hawthorne, NY) was present in the solution. In order to obtain reliable K and a values, the flow times of each solution were determined for various exposure times in the hot tetralin and then extrapolated back to zero exposure time. We note that trans 1,4 PBD also showed this time-dependent degradation, but syndiotactic 1,2 PBD samples showed negligible degradation in 135°C tetralin over the course of approximately 30 minutes.

Figures 1 and 2 are plots of η_{sp}/c and $\ln(\eta_r)/c$ as a function of concentration for all of the standards. Figure 3 is the best-fit regression plot of $\log [\eta]$ as a function of $\log M$, and it yields K and a equal to 0.0161 ± 0.0025 ml/g and 0.74, respectively, for analysis based on the η_{sp} correlation, and K and a equal to 0.0145 ± 0.0022 ml/g and 0.75 for analysis based on the $\ln(\eta_r)$ correlation. The plotted line on this figure is the average of the two sets of points. In either case, correlation coefficients (R^2) are greater than 0.992. Correlation coefficients for determination of $[\eta]$ values in Figures 1 and 2 are not as good, but analysis based on η_{sp} gives better correlation

coefficients than analysis based on $\ln(\eta_r)$. Our results are summarized in Table 2 along with literature values of K and a for PBD determined under various other experimental conditions.

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Table 1: Sample Concentrations

<u>M (g/mol)</u>	<u>Concentrations (g/ml)</u>
5,000	0.0021, 0.0052, 0.0073, 0.0082, 0.0127, and 0.0203
23,000	0.0010, 0.0022, 0.0043, 0.0082, and 0.0124
150,000	0.0010, 0.0025, 0.0039, 0.0052, and 0.0060
240,000	0.0010, 0.0020, 0.0030, and 0.0041

Composition	Conditions	K (ml/g)	α	Ref.
97% trans 1,4, 3% 1,2	toluene, 30°C, 50k-160k g/mol	0.0294	0.753	[5,6]
55% trans, 35% cis 1,4, 10% 1,2	toluene, 25°C	0.0142	0.80	[5,7]
51% trans, 43% cis 1,4, 6% 1,2	toluene, 30°C, 100k-250k g/mol	0.039	0.713	[5,8]
5.3% trans 1,4, 94.3% 1,2	toluene, 25°C	0.0901	0.81	[5,9]
50% trans, 42% cis 1,4, 8% 1,2	tetralin, 135°C, 5k-240k g/mol			
	η_r correlation	0.0145	0.75	
	η_{sp} correlation	0.0161	0.74	

Table 2: K and α Values for 1,4 Polybutadiene

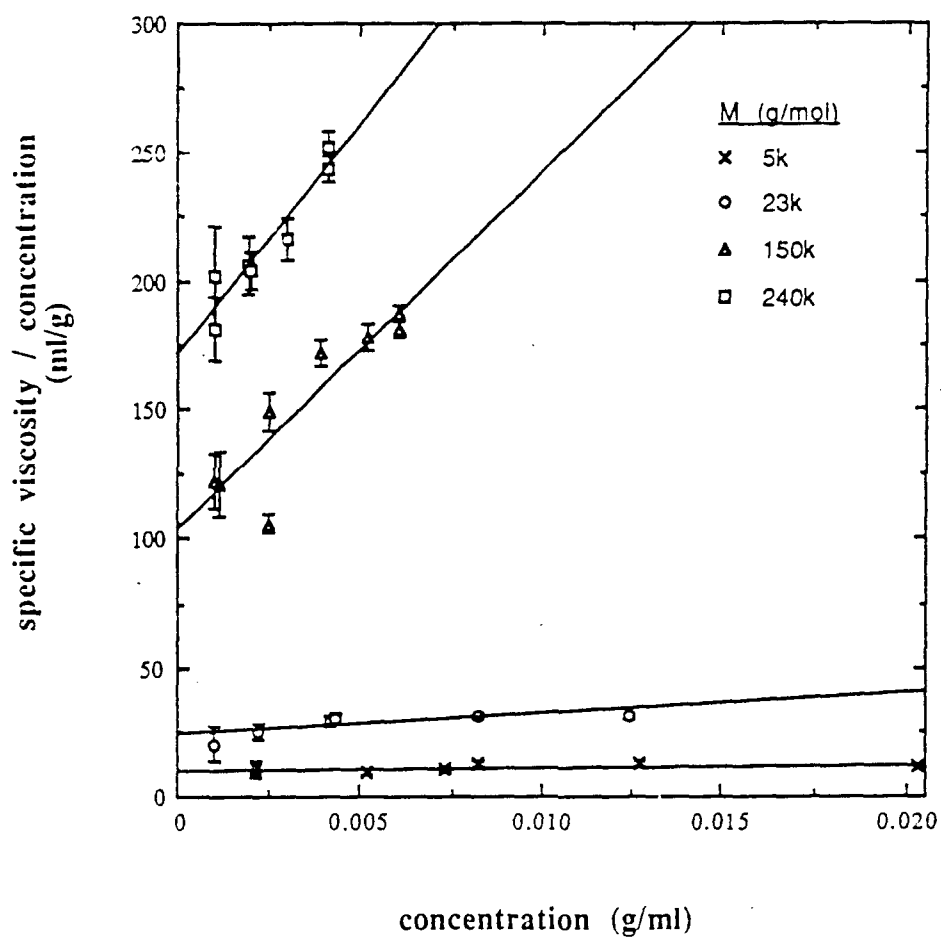


Figure 1: Specific Viscosity of 1,4 PBD Standards

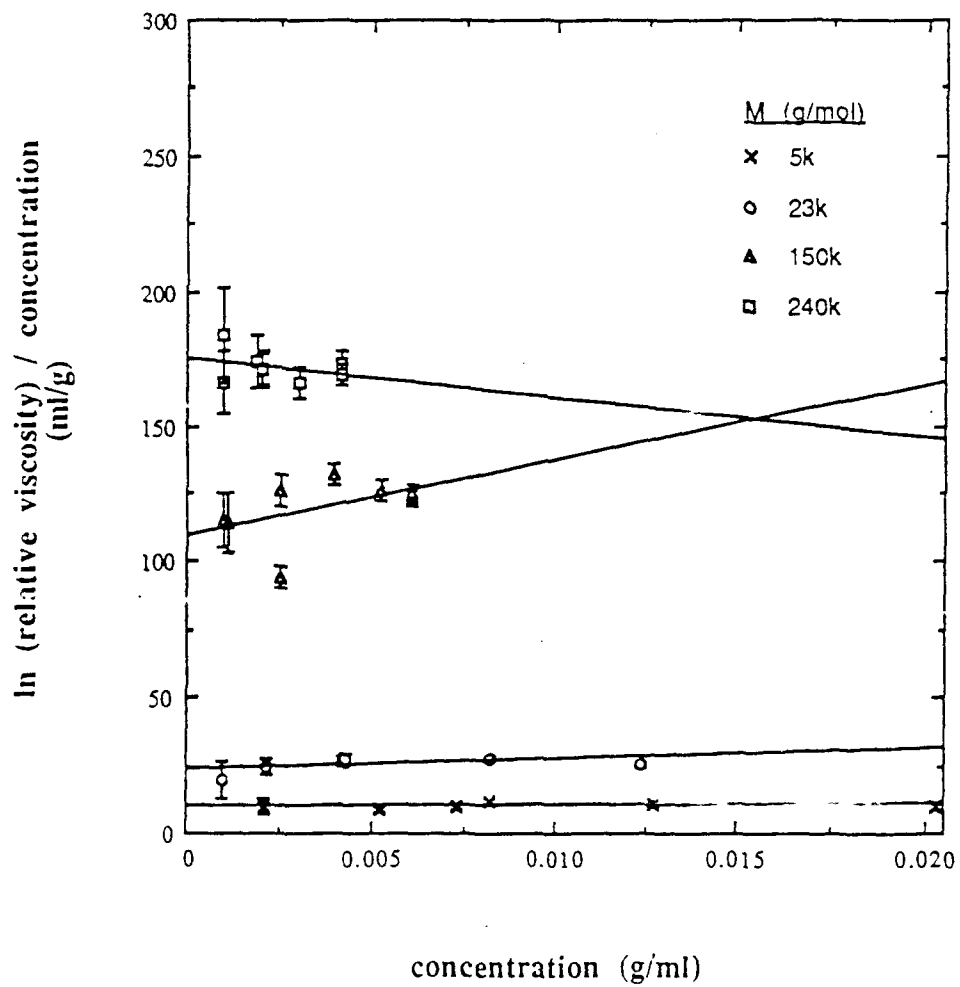


Figure 2: Relative Viscosity of 1,4 PBD Standards

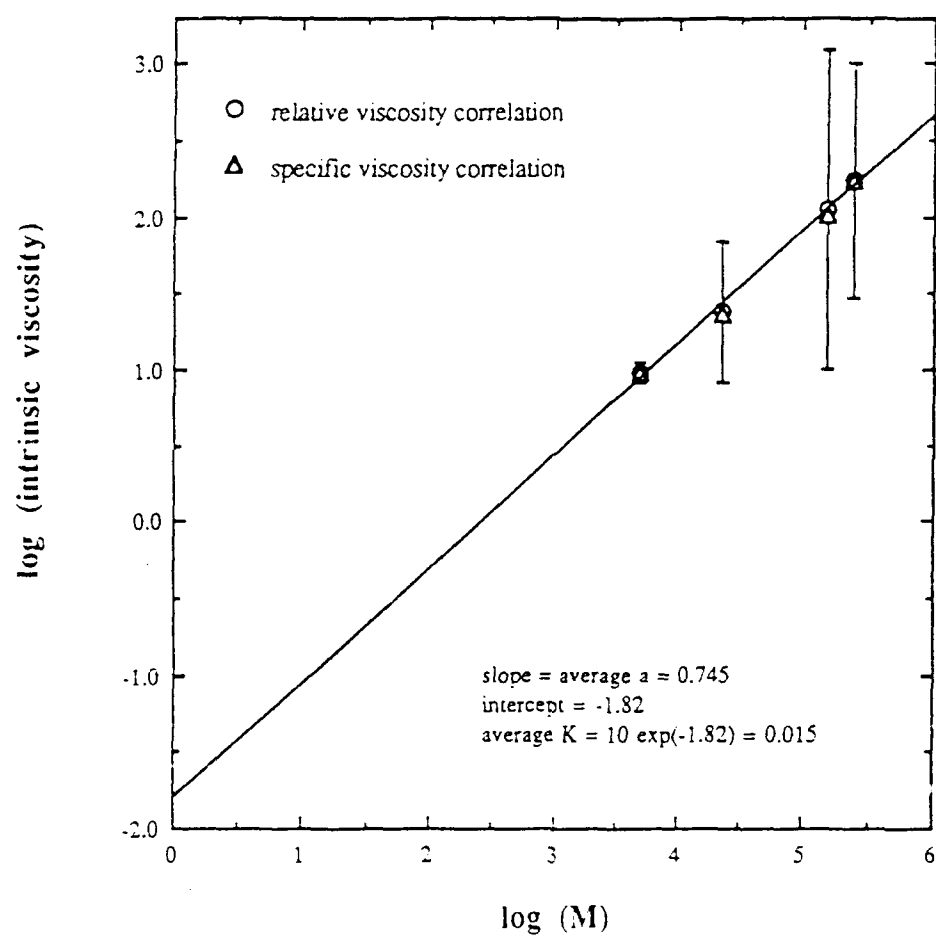


Figure 3: Regression Plot for Determination of Mark-Houwink Parameters